IR Spectroscopy: Fundamentals and Applications

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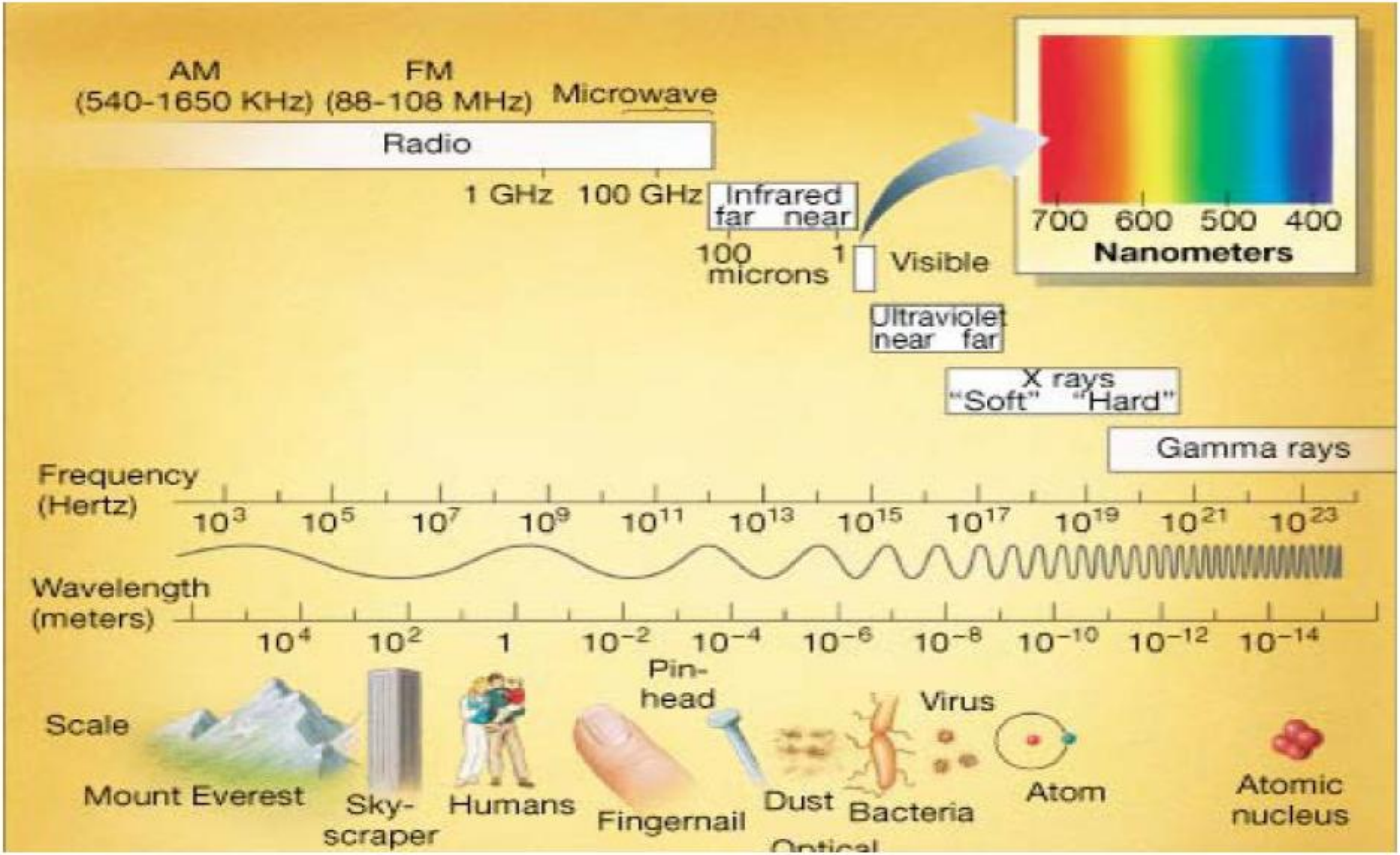
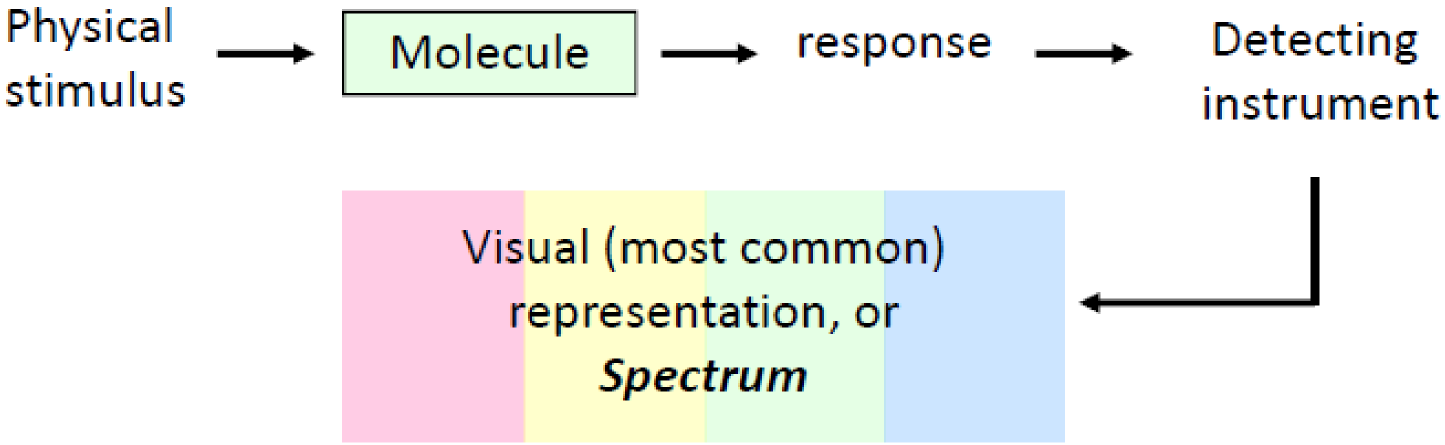
Wide Range of Types of Electromagnetic Radiation in nature.

- Only a small fraction (350-780 nM is visible light).
- The complete variety of electromagnetic radiation is used throughout spectroscopy.
- Different energies allow monitoring of different types of interactions with matter.
- $E=h\nu= hc/\lambda$


AM
(540-1650 KHz)
FM
(88-108 MHz)
Microwave
Radio
1 GHz
100 GHz
Infrared
far near
100 microns
1
Visible
700 600 500 400
Nanometers
Ultraviolet
near far
X rays
"Soft" "Hard"
Gamma rays
Frequency (Hertz)
10^3 10^5 10^7 10^9 10^{11} 10^{13} 10^{15} 10^{17} 10^{19} 10^{21} 10^{23}
Wavelength (meters)
10^4 10^2 1 10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-10} 10^{-12} 10^{-14}
Scale
Mount Everest
Sky-scraper
Humans
Fingernail
Pin-head
Dust
Bacteria
Virus
Atom
Atomic nucleus
Optical

SPECTROSCOPY - Study of spectral information

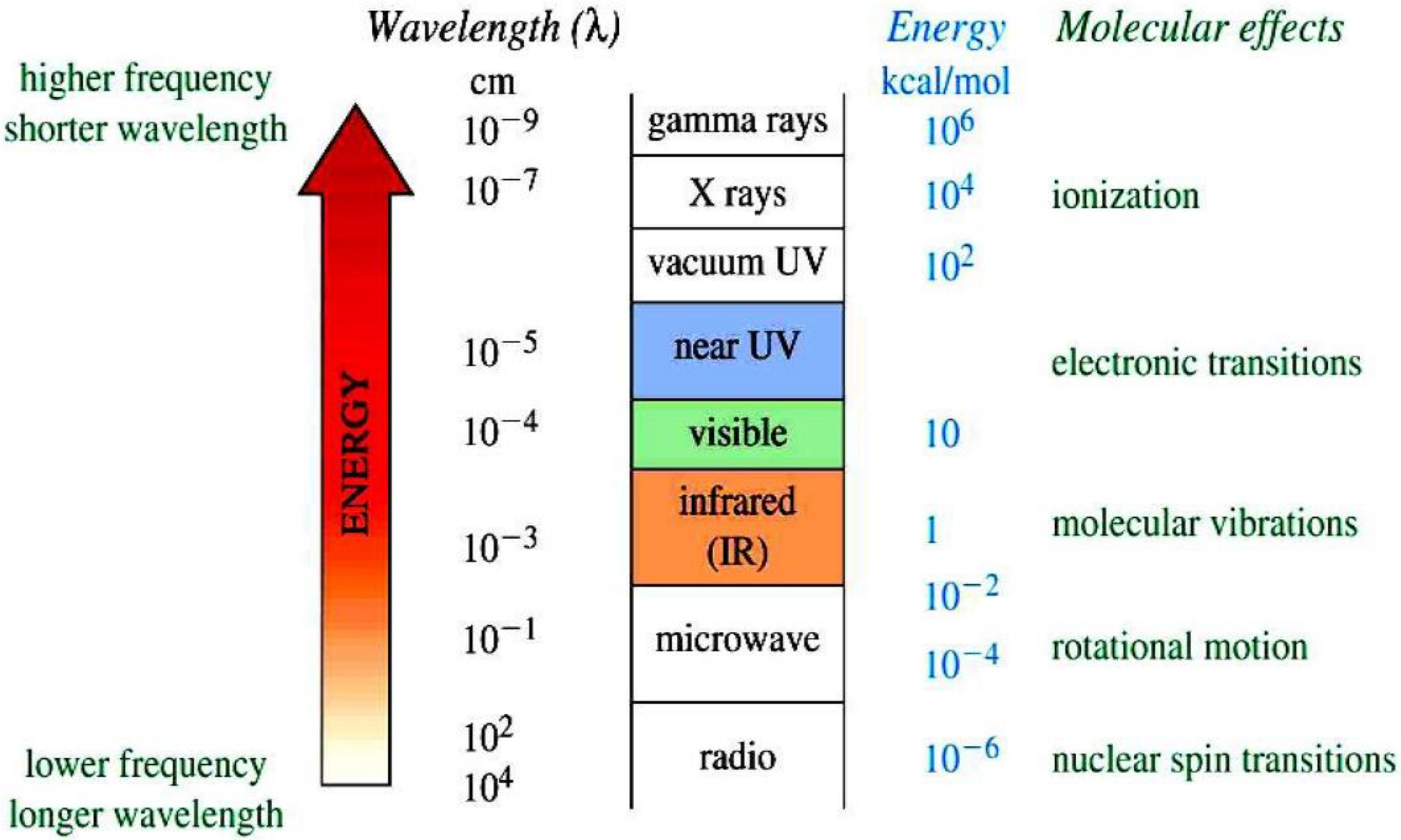


Physical stimulus → Molecule → response → Detecting instrument

Visual (most common) representation, or ***Spectrum***

Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



higher frequency
shorter wavelength

ENERGY

lower frequency
longer wavelength

Wavelength (λ)
cm
10^{-9}
10^{-7}
10^{-5}
10^{-4}
10^{-3}
10^{-1}
10^{2}
10^{4}

gamma rays
X rays
vacuum UV
near UV
visible
infrared (IR)
microwave
radio

Energy
kcal/mol
10^{6}
10^{4}
10^{2}
10
1
10^{-2}
10^{-4}
10^{-6}

Molecular effects
ionization
electronic transitions
molecular vibrations
rotational motion
nuclear spin transitions

The unit used on an IR spectrum is
Wavenumbers $\bar{\nu}$

$$\bar{\nu} = \text{wavenumbers (cm}^{-1}) = \frac{1}{\lambda}$$

wavelength (cm)

ν = frequency = $\bar{\nu}\,c$

C = speed of light
= 3×10^{10} cm/sec

or

$$\nu = \left(\frac{1}{\lambda}\right) c = \frac{c}{\lambda}$$

$$\frac{\text{cm/sec}}{\text{cm}} = \frac{1}{\text{sec}}$$

wavenumbers are directly proportional to frequency

RANGE OF IR

- Near IR: 0.8 to 2.5μm (12000cm^{-1}–4000cm^{-1})
- Analyzing mixtures of aromatic amines
- Determination of protein, fat, moisture, oil content.

- Middle IR: 2.5 to 15μm (4000cm^{-1} – 667cm^{-1})
- Also known as vibration- rotation region.
- This region is divided into:

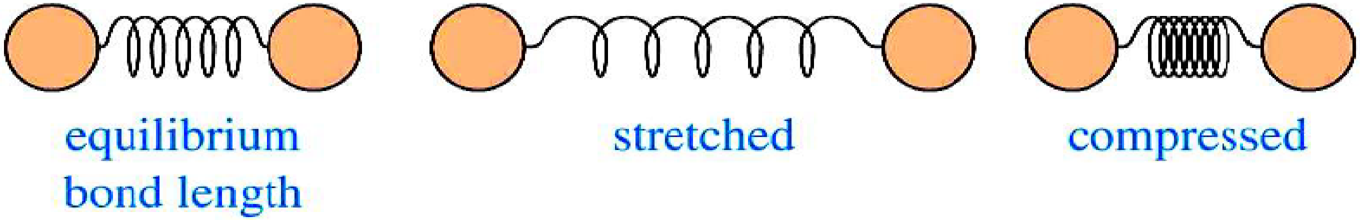
1. *Group frequency region*: **4000cm^{-1} – 1500cm^{-1}**
2. *Fingerprint region*: **1500cm^{-1} – 667cm^{-1}**

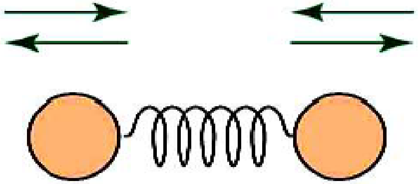
- Far IR: 15 to 1000μm (667cm^{-1} –10cm^{-1})
- Study of inorganic or organometallic compounds
- Sensitive to changes in overall structure of the molecule

Principle of IR spectroscopy

Infrared radiation is largely thermal energy.
It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

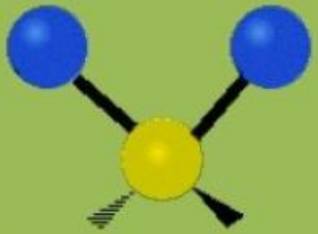
Specific bonds respond to (absorb) **specific** frequencies



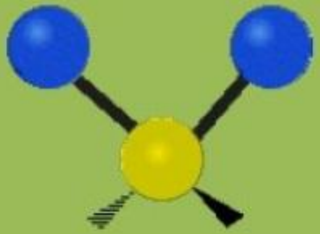


Type of Molecular Vibration

- **Stretching Vibrations**: in which bond length changes that require more energy.

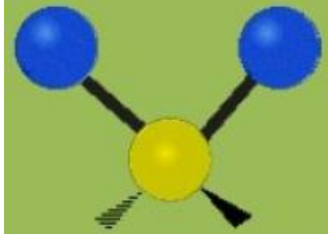


Symmetrical stretching

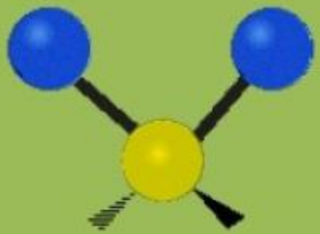


Asymmetrical stretching

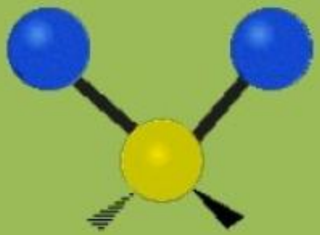
- **Bending Vibrations**: in which bond angle changes that require less energy.



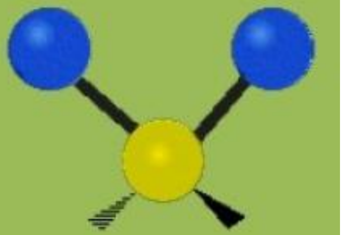
Rocking



Twisting



Scissoring



Wagging

Types of vibrations

Stretching Vibrations

Symmetrical

Asymmetrical

Bending Vibrations

Scissoring

Rocking

Twisting

Wagging

In plane

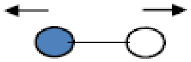
Out of plane

Number of Vibrational Modes

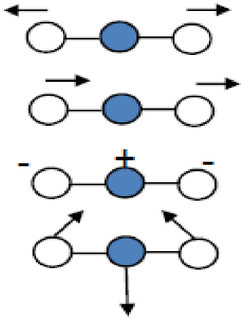
- The no. of Vibrational **degrees of Freedom (DOF)**
- Every atom in a molecule has 3 DOF in three Cartesian coordinates which defines its position in space.
- 3n= Vibrational DOF + Translational DOF +Rotational DOF (where n=No. of atoms)
- We have to calculate Vibrational DOF:
- **For linear molecules**, number of types of vibrations:
- 3n= Vibrational DOF + Translational DOF (3) +Rotational DOF (2)
- Vibrational DOF= 3n-3-2 =3n-5
- **For non-linear molecules**, number of types of vibrations:
- 3n= Vibrational DOF + Translational DOF (3) +Rotational DOF (3)
- Vibrational DOF= 3n-3-3 =3n-6

Examples:

1) HCl: 3(2)-5 = 1 mode



2) CO_2: 3(3)-5 = 4 modes



moving in-out of plane

3) C_6H_6: 3n-6=3(12)-6=30

❖why so many peaks in IR spectra?

- Overtones (2x, 2y), Combination (x+y. x+2y, 2x+y) and Difference bands (x-y. 2x-y, 2y-x etc.): 10-100 times less intense than fundamental

❖ observed vibration can be less then predicted because:

- symmetry (no change in dipole)
- energies of vibration are identical
- absorption intensity too low
- frequency beyond range of instrument

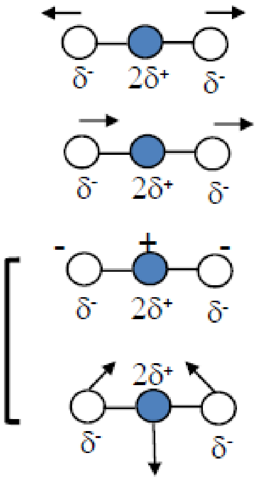
IR Active Vibrations:

- In order for molecule to absorb IR radiation:
- vibration at same frequency as in light.
- but also, must have a change in its net dipole moment as a result of the vibration.

Examples:

1) CO_2: 3(3)-5 = 4 modes

degenerate –identical energy single IR peak

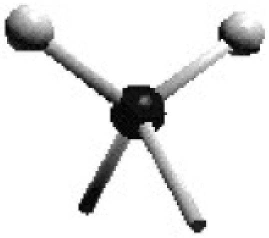


$\mu = 0$; IR inactive

$\mu > 0$; IR active

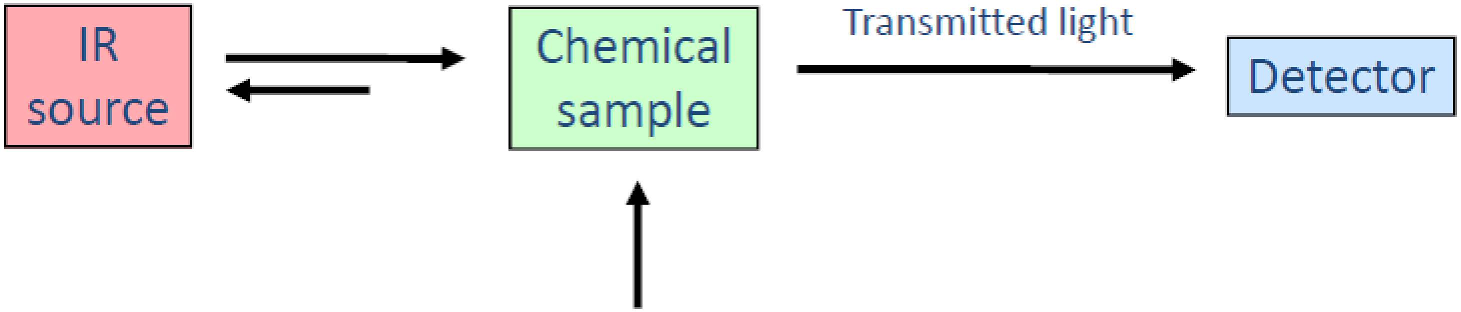
$\mu > 0$; IR active

$\mu > 0$; IR active



Transmission /Absorption

When a chemical sample is exposed to the action of **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.

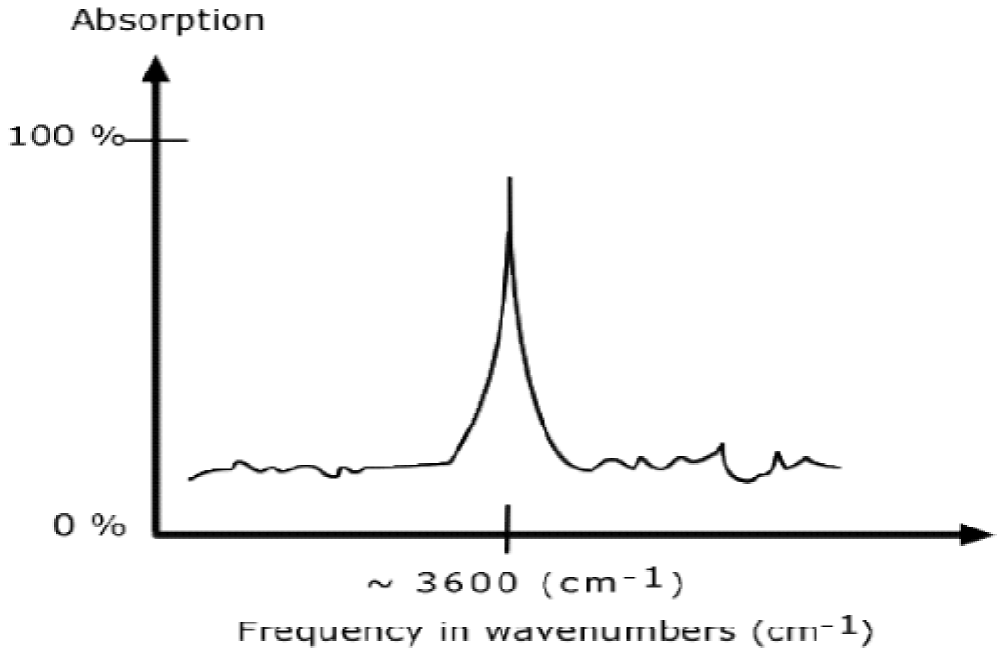


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

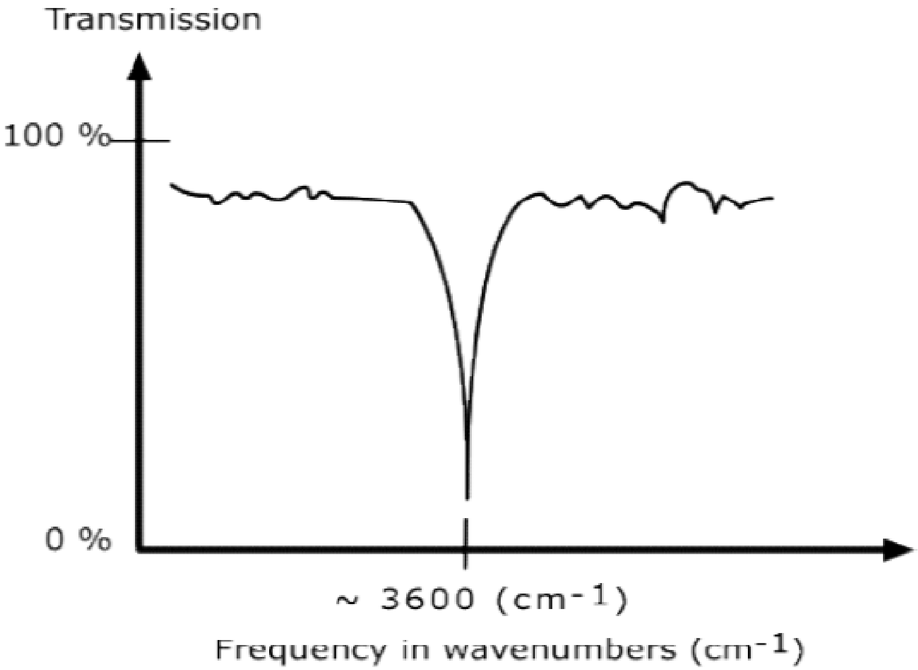
IR spectrum in Absorption mode

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.



The graph above shows a spectrum in **absorption** mode.

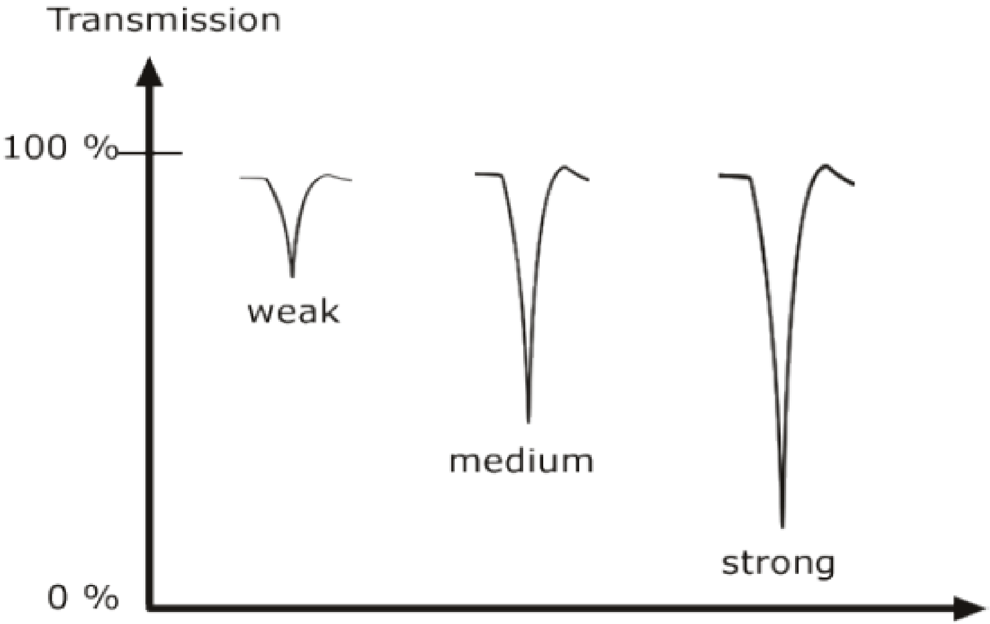
IR spectrum in Transmission mode



The graph above shows a spectrum in **transmission** mode.
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

Classification of bands

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.

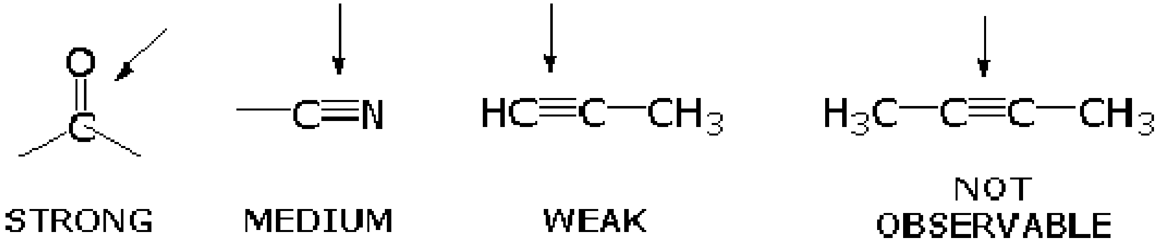


Infrared active bonds

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active.**

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

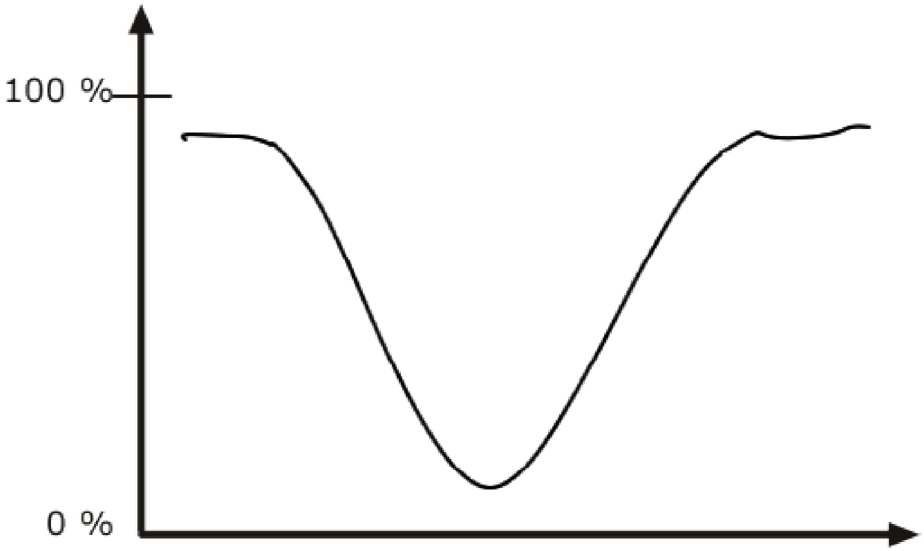
- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



Infrared band shapes

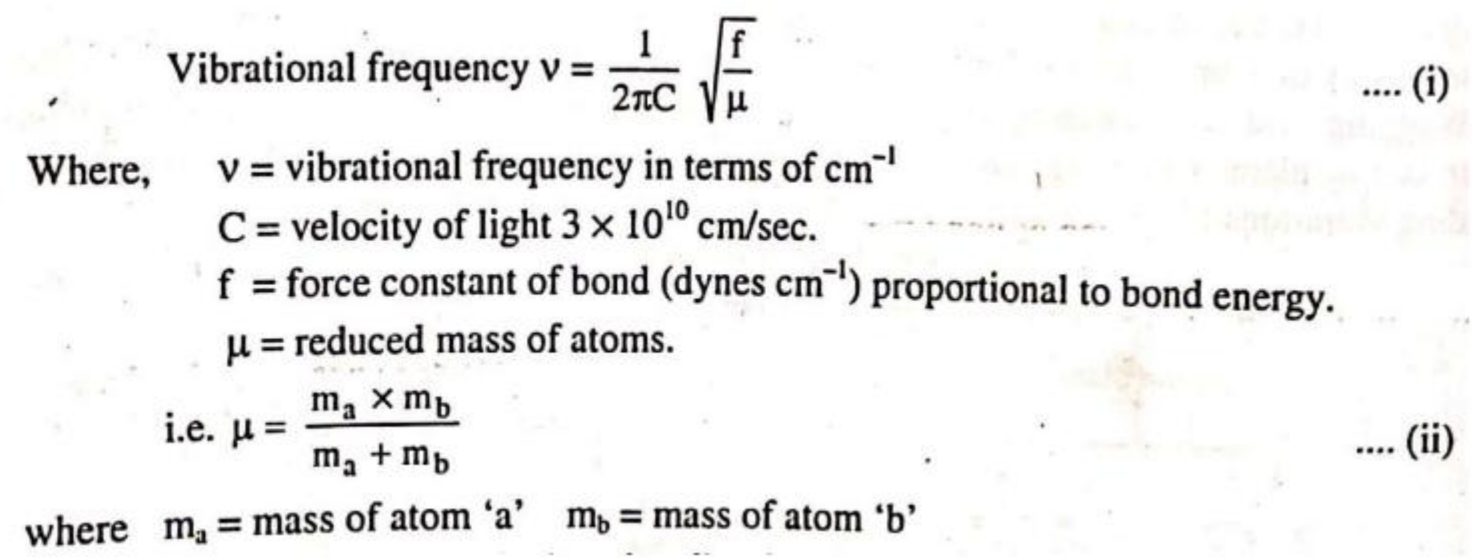
Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



Hooke’s Law

- Vibrational frequency of a bond is related to the masses of vibrating atoms and the force constant (f) of the vibrating bond.



$$\text{Vibrational frequency } \nu = \frac{1}{2\pi C}\sqrt{\frac{f}{\mu}} \qquad \text{.... (i)}$$

Where, ν = vibrational frequency in terms of cm^{-1}

C = velocity of light 3×10^{10} cm/sec.

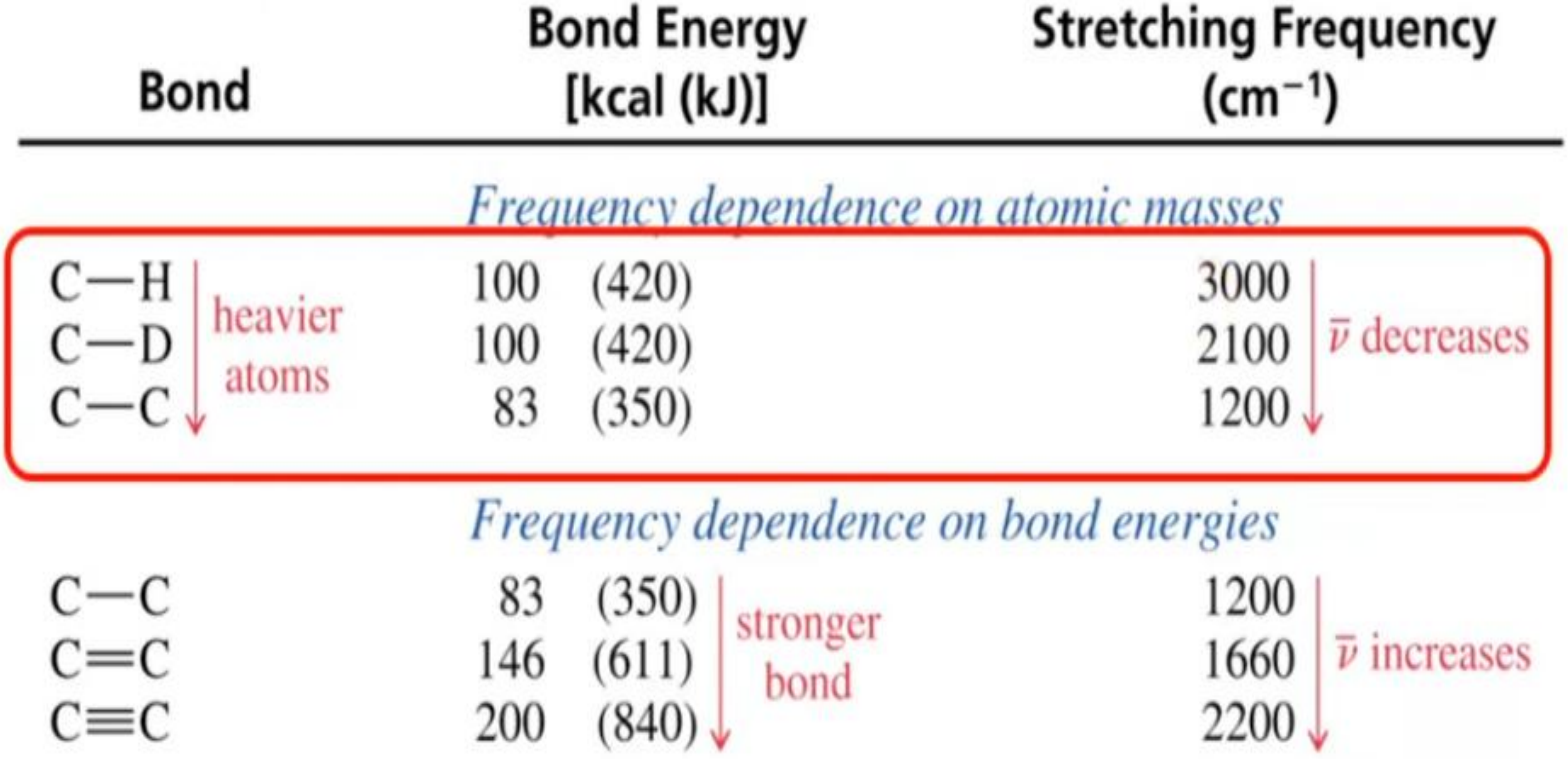
f = force constant of bond (dynes cm^{-1}) proportional to bond energy.

μ = reduced mass of atoms.

$$\text{i.e. } \mu = \frac{m_a \times m_b}{m_a + m_b} \qquad \text{.... (ii)}$$

where m_a = mass of atom ‘a’ m_b = mass of atom ‘b’

- **The stretching frequency depends on atomic weight and bond energy.**
  - **Frequency decreases with increasing atomic weight.**
  - **Frequency increases with bond energy.**



Bond		Bond Energy [kcal (kJ)]		Stretching Frequency (cm^{-1})	
		Frequency dependence on atomic masses			
C—H		100 (420)		3000	
C—D	heavier atoms	100 (420)		2100	$\bar{\nu}$ decreases
C—C		83 (350)		1200	
		Frequency dependence on bond energies			
C—C		83 (350)		1200	
C═C		146 (611)	stronger bond	1660	$\bar{\nu}$ increases
C≡C		200 (840)		2200	

Vibrational frequency or wave number depend upon following:

1. BOND STRENGTH

The frequency of vibration will be directly proportional to strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

	$C \equiv C$	$C=C$	$C-C$
Frequency=	2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

$\longleftarrow$

2. MASS

: Vibrational frequency is inversely proportional to the masses at the ends of the bond.

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000	1200	1100	750	600	500 Cm^{-1}

$\longleftarrow$

3. Hybridization:

- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

$SP > SP^2 > sp^3$

$3300\ CM^{-1}$ $3100\ CM^{-1}$ $2900\ CM^{-1}$